The Dynamics of Hydrogen Abstraction Reactions: Crossed-beam reaction Cl+n-C$_5$H$_{12}$→ C$_5$H$_{11}$+HCl
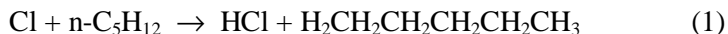
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Metathesis reactions, in which a single atom is transferred from a stable molecule to an atom or radical, are the only truly bimolecular (i.e. bimolecular in both directions) gas phase reactions[1]. Those involving hydrogen atom transfer arguably represent the most important subclass of this vast body of reactions, particularly for combustion dynamics. Free radical abstraction of hydrogen atoms in saturated hydrocarbons, for example, are reactions of great importance in combustion, and the differing propensities for reaction of primary, secondary, or tertiary H atoms, as well as the different dynamics underlying these pathways, are important to a detailed understanding of combustion chemistry. These processes have come under increasing scrutiny in recent years as experimental innovations have allowed more direct probing of the dynamics.

We have used reaction of Cl atoms with saturated hydrocarbons as a step toward a detailed investigation of these metathesis reactions. Our initial studies focused on the slightly exoergic reactions of Cl with propane (C$_3$H$_8$), with probe of the C$_3$H$_7$ product using synchrotron radiation[2]. The use of tunable undulator radiation, offering a unique combination of universality and selectivity in product detection, enables us to probe the doubly differential cross sections for the hydrocarbon radical fragment. The propane studies suggested different dynamics for the forward and backward scattered products. The former were ascribed to facile abstraction of the secondary H atoms, while the latter were believed to result from more strongly coupled collisions involving the terminal H atoms. Here we extend these studies to reaction of Cl with n-pentane[3], in an effort to examine the underlying trends in the reaction dynamics, in particular allowing us to probe the role of the extended carbon skeleton in these reactions.

These experiments were performed using a rotatable source molecular beam apparatus, Endstation 1, on the Chemical Dynamics Beamline[4] at the Advanced Light Source at Lawrence Berkeley National Laboratory. The apparatus has been described in detail elsewhere[5]. Briefly, a molecular beam of the hydrocarbon reagent, n-pentane, crosses a chlorine atom beam and the reactive scattering products are detected by a quadrupole mass spectrometer. The two molecular beam sources are fixed at 90° and the whole source chamber is rotatable to allow data collection at angles of -20° to 110° between the pentane beam and detector. The significant feature in the experimental setup is the use of the VUV undulator radiation for photoionization probe of the neutral scattering products, in place of the conventional electron impact ionizer. Detection of the scattered C$_5$H$_{11}$ reaction products was accomplished using 9.5 eV photoionization radiation with a MgF$_2$ filter that has transmission cutoff at about 11 eV, thus removing any residual radiation above that energy. The ionization potential (IP) of n-pentane is 10.35 eV, while for the pentyl radical it is 7.7 eV. By using a photoionization energy of 9.5 eV there is almost no background from dissociative ionization of the C$_5$H$_{12}$ reactant. A multichannel scaler triggered by the chopping wheel was used to record TOF at various laboratory scattering angles, defined with respect to the pentane beam. The center-of-mass translational energy and angular distributions were obtained by the forward convolution technique.

The reaction of chlorine atoms with n-pentane proceeds via either primary or secondary H atom abstraction:

$$Cl + n\text{-}C_5H_{12} \;\rightarrow\; HCl + H_2CH_2CH_2CH_2CH_2CH_3 \qquad (1)$$

$$Cl + n\text{-}C_5H_{12} \;\rightarrow\; HCl + H_3CHCH_2CH_2CH_2CH_3 \qquad (2)$$

$$Cl + n\text{-}C_5H_{12} \;\rightarrow\; HCl + H_3CH_2CHCH_2CH_2CH_3 \qquad (3)$$

Reactions 2 and 3 will be considered together since they both represent secondary H atom abstraction and are energetically indistinguishable.
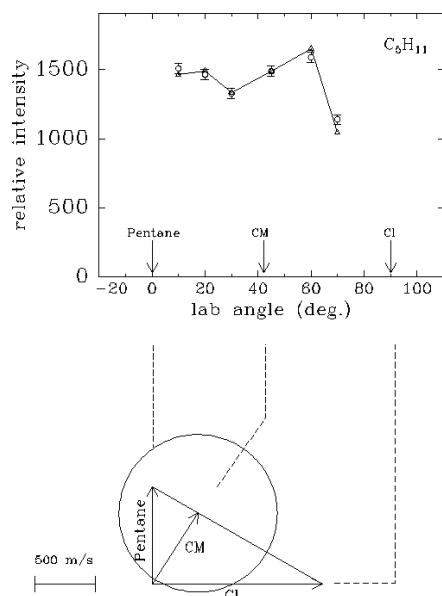

Figure 1. Lab angular distribution (top) and Newton diagram for the title reaction.

The Newton diagram for the reaction is shown in Fig. 1, along with the measured laboratory angular distribution. The maximum available energy for the 2-pentyl radical product from this slightly exothermic reaction gives the recoil limit circle indicated. Also shown in conjunction with the measured angular distribution is the simulated distribution resulting from the best fit to all of the data. The inherently coupled nature of the angular and energy distributions can be inferred directly from inspection of the angular distribution: the forward scattering extends beyond the beam in the forward direction, nearly to the recoil limit. The backscattered distribution, in contrast, drops sharply at a lab angle of 60°, well before the translational energy limit. This is confirmed by the time-of-flight distributions (not shown). These distributions serve to constrain the simulations from which the translational energy and angular distributions are obtained.

Although it was impossible to obtain a satisfactory fit to the data with a single uncoupled translational energy (P(E)) and angular distribution (T(Θ)), excellent fits were obtained simply by decomposing the center-of-mass distributions into two components, one forward and the other backward-scattered. The average energy release obtained for channel 1 (forward scattered) is $<E>_1=$ 20.4 kcal/mol, which is 92% of the available energy (E_{avail}), while for channel 2 (back-scattered) it is $<E>_2=$7.7 kcal/mol, which is 35% of E_{avail}. The branching fractions are 58% for channel 1 and 32% for channel 2. As in any forward convolution simulation of crossed-molecular beam results, the fit obtained is not unique. Nevertheless, the velocity-flux contour map we obtain, shown in Fig. 2, does faithfully reproduce the measured distributions. However, for the forward-scattered products in particular the decomposition into two components is somewhat arbitrary, and driven by the fit to the backscattered distribution.

The dynamics for the forward-scattered channel obtained from the fit are largely consistent with previous studies of Cl-hydrocarbon reaction dynamics. The P(E) peaks at the maximum energy available for formation of the isoenergetic 2-pentyl (butyl-1-methyl) or 3-pentyl (propyl-1-ethyl) radicals, with an average of only 1.8 kcal/mole remaining in rotation and vibration of the products. The bulk of the forward scattered distribution appears at translational energies exceeding the limit for formation of the 1-pentyl radical (the inner circle in Fig. 2). Abstraction of primary H atoms is thus ruled out for channel 1; however, there is little here to suggest any different propensities for abstraction of the hydrogen atoms from the 2- or 3- carbons.

The results for this channel are reminiscent of those reported for the Cl-cyclohexane reaction, and identified by others in propane and even for vibrationally excited methane. That is, the products are formed with very little internal energy. This has been attributed this to a collinear transition state; yet the correlation between forward scattering and a collinear transition state is problematic. Zare and coworkers[6] considered several possible mechanisms that could reconcile these, but finally suggested an alternative interpretation of the dynamics. They argued that if the reaction is not in the impulsive limit, then a cold product rotational distribution need not imply a collinear transition state. Accordingly, we suggest the coincident observation of a cold rotational distribution with forward scattering argues for a fairly loose transition state.

The dynamics for channel 2, the backscattered distribution, diverge dramatically from previous work on H abstraction dynamics in hydrocarbons, even differing significantly from our own studies of the analogous Cl-propane reaction. The P(E) for channel 2 peaks at 6.8 kcal/mol, with an average release of 7.7 kcal/mol, a fractional energy release of only 35%. This may be compared to results for Cl-propane, for which the fractional energy release for the backscattered component ranged from 52% at 11.5 kcal/mol collision energy to 48% at the highest 31 kcal/mol collision energy. This means that an average of 15 kcal/mol remains in internal degrees of freedom of the products. State-resolved studies for propane have shown only a small yield of vibrationally excited HCl product, so it is unlikely that this accounts for much of the energy. Furthermore, we anticipate little difference between the HCl energy content from propane or pentane, since the energetics are virtually the same for both reactants. The likely repository of the bulk of this energy is thus in the hydrocarbon fragment; the question is whether it is in rotation or vibration. Plausible reasons for greater vibrational excitation in the case of pentane vs. propane are readily apparent. There are many more vibrational modes for n-pentane (45 vs. 27), and perhaps more significantly, many more involving the low-frequency C-C-C bends. For these modes, with vibrational frequencies on the order of 800 cm^{-1}, the half-period is roughly 20 fs. We can compare this to the collision time under the conditions of the experiment: for an effective interaction region of 0.5 X at 2400 m/s we estimate a collision time of 21 fs, a remarkable match to the vibrational period. The combination of the higher density of states and the excellent match between the collision time and the bending mode vibrational period greatly favors coupling between the collision energy and the internal modes of the hydrocarbon. This suggests that in pentane we are seeing the direct participation of the extended carbon backbone in the reaction.

A final question concerns the nature of the two different channels. In our previous work on the propane reaction, we argued for the association of the forward-scattered distribution with the abstraction of secondary H atoms, while the backscattered product was associated with primary H atoms. It is even clearer in the pentane case, since the bulk of the forward scattered products are formed at translational energies well exceeding that possible for production of the 1-pentyl radicals, that the forward scattered products are indeed the result of secondary H atom abstraction. The question remains for the backscattered products: Are they preferentially associated with primary H abstraction? Although attempts were made to discriminate between these two radical isomers based upon their ionization potentials, we found no significant differences in the angular distributions as a function of probe photon energy. However, the vastly different internal energy distributions for the forward and backward scattered products may account for the absence of any significant differences, and would make interpretation of such an effect problematic in any case.

Although there is no direct evidence indicating a connection between the predominantly backscattered 'channel 2' and the primary abstraction channel, several lines of evidence point this direction. Firstly, the maximum energy release apparent in the contour map in Fig. 3, extends well below the limit of the available energy for production of the higher energy isomer. This distribution came directly from the best fit to the laboratory data and was in no way enforced. Secondly, there is the total branching between forward and backward scattered products. For the propane reaction, the fraction scattered forward of 90° was very close to 50% of the total. Assuming simply a limiting case

Figure 2. Contour map for pentyl radical derived from experiment. Forward scattering is to the left of the figure.

association of forward scattering with secondary H abstraction we find, effectively, three times higher reactivity of the secondary vs. primary H atoms. For pentane, then, we expect the fraction forward scattered to increase from 1/2 to 3/4, since there are three times the number of secondary
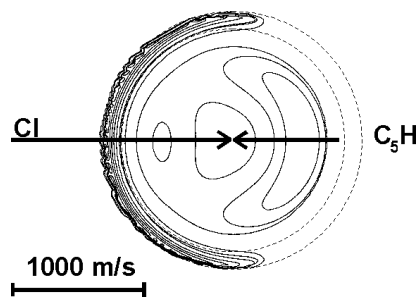
H atoms, if this limiting assumption is a good one. Indeed, if we look only at the fraction of the total scattered in the forward direction, in the same way we considered the propane case, we find a value of 74%, a remarkable agreement.   If we compare the fraction of the total scattered into 'channel 1', then the value is 64%. If we make the association between channel 1 and secondary H abstraction, and channel 2 and primary H abstraction, this implies roughly a 1.8-fold higher reactivity of the secondary H atoms. However, we cannot directly compare this to the propane results since the distributions were decomposed differently.

These translational energy distributions argue for a bit of caution on the part of those employing state-resolved laser methods relying on measurements of one of the fragments to extract the speed and angular distributions for the reaction. These studies are generally blind to internal energy in the undetected fragment. Moreover, the reconstruction of the product distributions require some assumptions about the unmeasured fragment. If these assumptions are in error, then the derived distributions are inaccurate. Usually the assumption is made that the undetected fragment is internally cold, although in at least one case this issue was considered explicitly. As we have seen, for the forward-scattered products in the pentane and propane case, this is a fairly accurate assumption. For the backscattered distributions, however, this is grossly incorrect. The implications of this for the inferred distributions are not clear, but these issues should be considered for any quantitative analysis of the photoloc-type experiments.

References
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